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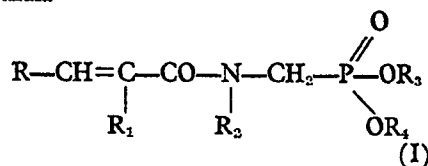


(54) N-ACYLAMINO-METHYL-PHOSPHONATES AND THEIR
 USE AS FLAME PROOFING AGENTS

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

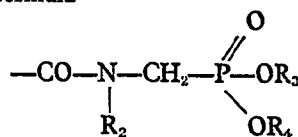
This invention relates to certain phosphonic acid derivatives, to a process for their production and to their use as flameproofing agents for textile materials, paper or plastics.

This invention provides a process for the preparation of an N - acylamino - methyl-phosphonic acid derivative of the general formula



in which

R represents hydrogen, a methyl group, a (C₁—C₄-alkoxy)carbonyl radical or a radical of the formula

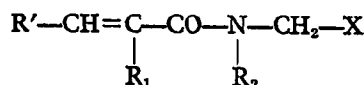


R₁ represents hydrogen or a methyl group, R₂ represents hydrogen, a C₁—C₄-alkyl radical which is optionally substituted by one or more hydroxyl groups and/or halogen atoms, or a C₃—C₄-alkenyl radical, and

R₃ and R₄ independently of one another represent hydrogen, an alkali metal, alkaline earth metal or ammonium ion, or a C₁—C₄-alkyl radical which is optionally substituted by one or more halogen atoms, or together with the oxygen atoms and the phosphorus

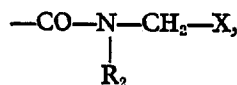
atom form a five-membered to seven-membered heterocyclic structure,

in which process an N - acyl - amino-methyl derivative of the general formula



in which

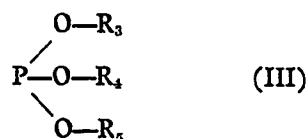
R' is hydrogen, a methyl group, a (C₁—C₄-alkoxy)carbonyl radical or a radical of the formula



R₁ and R₂ have the above-mentioned meanings, and

X represents a dimethylamino or diethylamino group or an acetoxy or propionyloxy radical or, preferably, a halogen atom, especially a chlorine atom, or a hydroxyl group,

is reacted with a phosphorous acid triester of the general formula



in which

R₃, R₄ and R₅ independently of one another represent a C₁—C₄-alkyl radical which is optionally substituted by one or more halogen atoms, or

R₃ and R₄ together with the oxygen atoms and the phosphorus atom form a five-membered to seven-membered heterocyclic structure,

optionally in the presence of an inert diluent, at temperatures of 40—160°C, preferably 60—130°C. When using N - acylamino-

methyl derivatives of the formula (III) in which X represents an acetoxy or propionyloxy radical, temperatures of 90—150°C have proved advantageous.

- 5 The compounds of the formula (I), where-
in R_1 and R_2 are hydrogen or alkali metal,
alkaline earth metal or ammonium ions, may
be prepared by conventional methods that are
well-known in the art, for example by hydroly-
10 sis of the alkyl esters of the formula (I),
optionally followed by neutralization.

- The present invention also provides, as new
compounds, the N - acylamino - methyl phos-
phonic acid derivatives of the formula (I), in
15 which R_1 , R_2 , R_3 and R_4 have the mean-
ings stated above, with the proviso that R_2
and R_4 cannot both be unsubstituted alkyl
when R_1 , R_3 and R_4 are all hydrogen.

- 20 Preferably, R is hydrogen, R_1 and R_2
are each hydrogen or methyl and R_3 and R_4
are each ethyl or chloroethyl.

- As examples of representatives of the phos-
phorous acid triesters of the formula (III)
there may be mentioned: trimethylphosphite,
25 triethylphosphite, dimethylethylphosphite, tri-
isopropylphosphite, tri - n - propylphosphite,
dimethyl - n - propylphosphite, tri - n -
butylphosphite, tri - isobutylphosphite, tris-
(chloroethyl) - phosphite, tris - (bromo-
30 ethyl) - phosphite, 2 - methoxy - 1,3 -
dioxo - phospholane and 2 - ethoxy - 4 -
methyl - 1,3 - dioxo - phospholane.

- As examples of representatives of the N -
acyl - amino - methyl compounds of the
35 formula (II) there may be mentioned: N -
chloromethyl - N - methyl - acrylic acid
amide, N - chloromethyl - N - methyl - meth-
acrylic acid amide, N - (acetoxy - methyl) -
methacrylic acid amide, N - (propionyloxy-
40 methyl) - methacrylic acid amide, N - chloro-
methyl - N - methyl - crotonic acid amide,
N - chloromethyl - N - methyl - fumaric
acid methyl ester amide, N,N' - bis - chloro-
methyl - N,N' - dimethyl - fumaric acid
45 diamide, N - bromomethyl - N - methyl-
acrylic acid amide, N - (N',N' - diethyl-
amino - methyl) - methacrylic acid amide,
N - hydroxymethyl - acrylic acid amide, and
N - hydroxymethyl - methacrylic acid amide.

- 50 In the reaction, according to the invention,
of the compounds of the formula II with the
phosphorous acid triesters of the formula
III it is advisable continuously to remove the
compound R_1X produced in the reaction, for
55 example methyl chloride, ethyl bromide or
methyl acetate, from the reaction mixture,
for example by distillation or by means of
a stream of inert gas. In general, the com-
pounds of the formulae II and III are em-
60 ployed in equimolar amounts, but the phos-
phorous acid triesters III can also be used in
slight excess. (Molar ratios of 1:1 to 1:2).

- If appropriate, inert diluents, such as
65 toluene, xylene, n - nonane or dimethylform-
amide can be used conjointly in the reaction.

It should be pointed out that the reaction
of the compounds of the formula II in which
X represents an acetoxy or propionyloxy
radical, with the phosphorous acid triesters of
the formula III represents a new, chemically
70 peculiar reaction.

The compounds of the formula I are cap-
able of numerous uses. Thus, for example, new
compounds with valuable properties can be
obtained by addition of compounds with active
75 hydrogen atoms to the double bond of the
compounds of the formula I. For example,
the addition of long-chain amines to the
double bond produces surface-active com-
pounds from which compounds having a bac-
80 tericidal action can be obtained by alkylation
or saponification.

The compounds of the formula I can
furthermore be polymerised in the usual man-
ner, or be reacted with other polymerisable
85 monomers to give copolymers. The compounds
of the formula I are suitable for use as
flameproofing agents for textiles of natural
or synthetic fibre materials, for example of
cotton or regenerated cellulose, polyesters,
90 natural or synthetic polyamides or polyacrylo-
nitrile or their mixtures, and for other materials
for example paper and plastics.

Thus, the present invention provides a
method of flameproofing a textile, paper or
95 plastics material, which comprises incorporat-
ing into the said material a compound
according to this invention.

For flameproofing the materials, the pre-
sent compounds, preferably together with radical
100 donors, such as ammonium persulphate,
are applied to the materials, for example
from aqueous baths, and subsequently sub-
jected to a heat treatment at 120—200°C
or to the action of ionising radiation. Other
105 polymerisable monomers, preferably acryl-
amide, N - methylol - acrylamide or N -
methoxymethyl - acrylamide, can be used
conjointly in this treatment.

The parts indicated in the examples which
110 follow are parts by weight, unless stated other-
wise.

Example 1

83 parts of triethylphosphite are mixed
with 0.5 part of copper powder and heated
115 to 70—80°C. 74 parts of N - chloromethyl-
N - methyl - methacrylic acid amide are added
dropwise at the same temperature. Ethyl
chloride was evolved in an exothermic reac-
tion and is collected in a cold trap cooled
120 with solid carbon dioxide. (Yield: 30 g).

After completion of the addition, the reac-
tion mixture is heated to 70—80°C for a
further hour. Thereafter, the almost colour-
less reaction mixture in the reaction vessel
125 is distilled in vacuo. Yield: 88 g of a
colourless liquid of refractive index n_D
1.4634; boiling point: 112—115°C/0.3 mm
Hg. The IR spectrum of the product agrees
with the structure.

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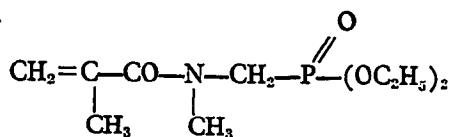
110

115

120

125

130



$\text{C}_{10}\text{H}_{20}\text{NO}_4\text{P}$ (molecular weight 249)

Calculated:

C: 48.23% H: 8.98% N: 5.62%

P: 12.43%

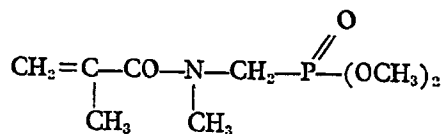
Found:

C: 47.4% H: 8.4% N: 5.8%

P: 11.9%.

Example 2

- 10 220 parts of trimethylphosphite and 0.5 part of copper powder are reacted, as described in Example 1, with 263 parts of crude N - chloromethyl - N - methyl - methacrylic acid amide at 60—70°C and the mixture is stirred for 1 hour at 70—80°C. The distillation of the reaction mixture yields 230 parts of a colourless liquid of refractive index n_D : 1.4729; boiling point: 108°C/0.1 mm Hg. The IR spectrum of the product agrees with the expected structure.



$\text{C}_8\text{H}_{16}\text{NO}_4\text{P}$ (molecular weight 221)

Calculated:

C: 43.44% H: 7.29% N: 6.33%

P: 14.01%

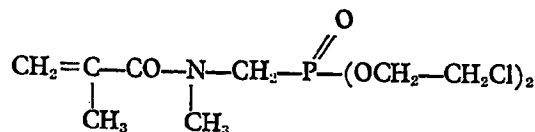
Found:

C: 44.1% H: 7.4% N: 6.7%

P: 13.5%.

Example 3

- 30 103 parts of trimethylphosphite and 0.5



$\text{C}_{10}\text{H}_{18}\text{NO}_4\text{PCl}_2$ (molecular weight 318)

Calculated:

N: 4.40% P: 9.73% Cl: 22.25%

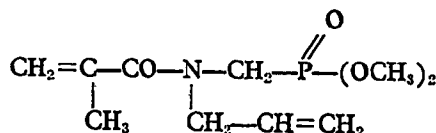
Found:

N: 4.04% P: 10.45% Cl: 23.40%.

Example 5

- 70 100 parts of triethylphosphite and 0.5 part of copper powder are heated to 80—90°C and 96 parts of N - methyl - N - chloro-

part of copper powder are reacted, as described in Example 1, with 132 parts of N - chloromethyl - N - allyl - methacrylic acid amide at 80—90°C. The distillation of the reaction mixture yields 82 parts of a liquid of refractive index n_D 1.4805. Boiling point: 117—119°C/0.25 mm Hg. The IR spectrum of the product agrees with the structure.



$\text{C}_{10}\text{H}_{18}\text{NO}_4\text{P}$ (molecular weight 247)

Calculated:

C: 48.58% H: 7.34% N: 5.67%

P: 12.53%

Found:

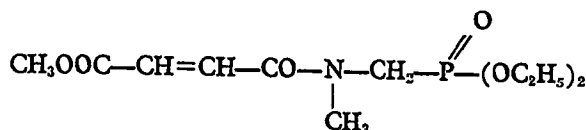
C: 49.1% H: 7.5% N: 5.9%

P: 11.9%.

Example 4

405 parts of tris - (2 - chloroethyl) - phosphite are heated to 100—110°C and 222 parts of N - chloromethyl - N - methyl-methacrylamide are added dropwise at the same temperature. At the same time, the dichloroethane formed is distilled off in a stream of nitrogen. After completion of the addition, the pressure is slowly reduced to 0.5 mm Hg, in the course of which the easily volatile constituents distil off. 458 parts of a yellowish viscous liquid, of which the IR spectrum agrees with the structural formula, are left.

methyl - fumaric acid methyl ester amide are added dropwise at this temperature. The resulting ethyl chloride is distilled off in a stream of nitrogen. After completion of the evolution of ethyl chloride, the pressure is lowered to 0.5 mm Hg and the temperature raised to 100—110°C and kept at this level until all easily volatile constituents have been distilled off. 138 parts of a reddish-coloured viscous liquid remain, of which the IR spectrum agrees with the structural formula.



$C_{11}H_{20}NO_6P$ (molecular weight 293)

Calculated:

P: 10.57% N: 4.78%

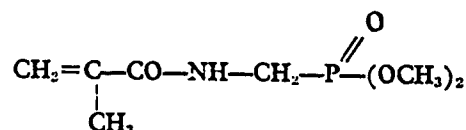
Found:

5 P: 10.45% N: 4.86%.

Example 6

720 parts of N - acetoxymethyl - methacrylic acid amide and 672 parts of trimethylphosphite are mixed at room temperature and 0.5 g of phenothiazine is added. About 200 ml of this mixture are heated in a flask, provided with a column heated to 60°C, a dropping funnel, a stirrer, a thermometer and a gas inlet tube, to 100—110°C until acetic acid methyl ester distils off. Whilst doing this, the apparatus is kept under nitrogen, using the gas inlet tube. The bulk of the mixture is then allowed to run in dropwise over the course of 2—3 hours and finally the mixture is heated to about 125°C until no further acetic acid methyl ester distils off. Excess trimethylphosphite is distilled off at 100°C/10—20 mm Hg. During the subsequent distillation of the residue, 615 g (76% of theory) of a colourless liquid of boiling point 170—180°C/1.2—1.5 mm Hg are obtained. The IR spectrum of the product agrees

with the indicated structural formula.



$C_7H_{14}NO_4P$ (molecular weight 207)

Calculated:

C: 40.5% H: 6.5% N: 6.5%

O: 30.6% P: 14.9%

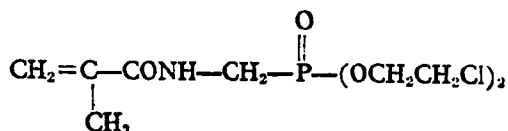
Found:

C: 40.5% H: 7.1% N: 6.4%

O: 30.4% P: 14.7%.

Example 7

71.5 parts of N - acetoxymethyl - methacrylic acid amide and 136 parts of tris - (2 - chloroethyl) - phosphite are mixed at room temperature and 0.2 part of phenothiazine is added. The mixture is introduced dropwise into a flask heated to 120—140°C, in the course of which the resulting acetic acid 2 - chloroethyl ester is distilled off at 20—30 mm Hg through a column heated to 70°C. After completion of the reaction, the volatile constituents are distilled off at 0.5 mm Hg and 130—140°C. 144 parts (95% of theory) of a viscous oil which cannot be distilled are left.



$C_9H_{16}NO_4PCl_2$ (molecular weight 304)

Calculated:

55 C: 35.4% H: 5.25% N: 4.6%

Cl: 23.3% P: 10.2%

Found:

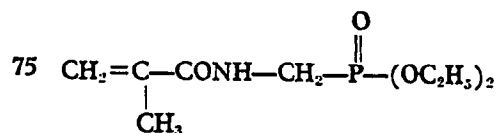
C: 35.4% H: 5.3% N: 4.3%

Cl: 23.0% P: 10.5%.

Example 8

A mixture, prepared at room temperature, of 164 parts of N - acetoxymethyl - methacrylic acid amide, 210 parts of triethylphosphite and 0.3 part of phenothiazine is allowed to run dropwise into a flask heated to 120—130°C. The acetic acid ethyl ester which forms is distilled off with the aid of a slight stream of nitrogen through a column heated to 80°C. After completion of the reaction, the excess phosphite is distilled off in vacuo and the residue is distilled.

Yield: 145 parts (62% of theory) of a colourless liquid; $n_D^{20}=1.4703$; boiling point: 160—170°C/0.7—1.0 mm Hg.



$C_9H_{18}NO_4P$ (molecular weight 235)

Calculated:

C: 46.0% H: 7.65% N: 5.95%

P: 13.2%

Found:

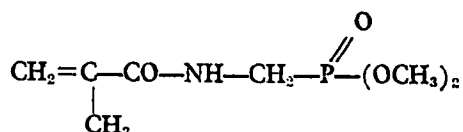
C: 46.3% H: 7.9% N: 6.4%

P: 13.5%.

Example 9

223 parts of trimethylphosphite and 4 parts of hydroquinone are heated to 105—110°C. 174 parts of fused N - hydroxymethyl - methacrylamide are added dropwise at the same temperature from a dropping funnel which can be heated, under a nitrogen atmosphere. At the same time, a mixture of methanol and trimethylphosphite is slowly distilled off through a column. After completion of the addition, the temperature is gradually raised to 130—135°C, until the distillation has ended. In total, approx. 50 parts of a methanol/trimethylphosphite mixture are distilled off. Thereafter the reaction mixture is freed of the easily volatile constituents in a water-pump vacuum at 120°C bath temperature. The lower-boiling constituents are subsequently distilled from the 313 parts of distillation residue in a thin layer distillation apparatus at 0.8 mm Hg and 120°C. Thereafter, 260

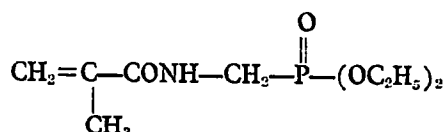
parts of distillation residue are left in the form of a viscous, slightly brownish liquid, which according to analysis by gas chromatography consists to the extent of 78% of the compound of the formula



described in Example 6.

Example 10

146 parts of triethylphosphite and 0.5 part of phenothiazine are heated to 120°C and 135 parts of N - (N',N' - diethylamino-methyl) - methacrylic amid amide are added at the same temperature. The temperature is slowly raised to 160°C, in the course of which 61 parts of an amine mixture of boiling point 69—89°C distil off. Fractional vacuum distillation of the residue yields 71 parts (30% of theory) of a compound boiling at 137—144°C/0.2 mm Hg, which according to examination by gas chromatography is identical with the compound of the formula



described in Example 8.

Example 11

Polyamide carpet material is impregnated with an aqueous liquor which per litre contains 300 g of the compound described in Example 6, 100 g of thiourea, 10 g of cerium nitrate and 1 g of a non-ionic wetting agent. The material is squeezed out to a weight increase of 130% and is dried at 100°C and heated to 120°C for 10 minutes. The flameproof finish thus obtained was tested by the Methenamine Test (DOC FF 2-70), and in particular the carpet material was tested a) after finishing and b) after shampooing three times with a commercially available carpet cleaning shampoo. The material withstood the flameproof test in both cases. An equivalent flameproof finished was also achieved with a treatment liquor which per litre contained 300 g of the compound described in Example 4, 100 g of thiourea, 50 g of acrylamide, 10 g of ammonium persulphate and 1 g of nonionic wetting agent.

Example 12

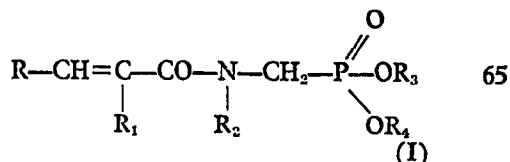
Cotton fabric is impregnated on a padder with an aqueous liquor which per litre contains 400 g of the compound described in Example 7, 300 g of acrylamide, 10 g of

ammonium persulphate, 4 g of sodium sulphite and 0.5 g of a non-ionic wetting agent, and is squeezed out to a weight increase of 110%. Thereafter the fabric is heated to 100°C for 60 minutes and is then rinsed in warm water and dried.

The flameproofing action of the finish was tested in the vertical test according to DIN 53,906. The fabric withstood the test after finishing even after 5 washing machine washes at 90°C.

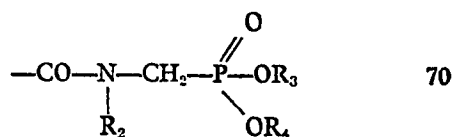
WHAT WE CLAIM IS:—

1. N - Acylamino - methyl - phosphonic acid derivatives of the general formula



in which

R represents hydrogen, a methyl group, a (C₁—C₄-alkoxy)carbonyl radical or a radical of the formula



R₁ represents hydrogen or a methyl group, R₂ represents hydrogen, a C₁—C₄-alkyl radical which is optionally substituted by one or more hydroxyl groups and/or halogen atoms, or a C₃—C₄-alkenyl radical, and

R₃ and R₄ independently of one another represent hydrogen, an alkali metal, alkaline earth metal or ammonium ion, or a C₁—C₄-alkyl radical which is optionally substituted by one or more halogen atoms, or together with the adjacent oxygen atoms and the phosphorus atom form a five-membered to seven-membered heterocyclic structure, with the proviso that R₃ and R₄ cannot both be unsubstituted alkyl when R, R₁ and R₂ are all hydrogen.

2. Compounds according to claim 1, in which R is hydrogen.

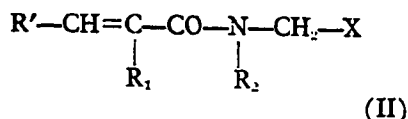
3. Compounds according to claim 1 or 2, in which R₃ and R₄ are identical and represent ethyl or chloroethyl radicals.

4. Compounds according to claim 1, 2 or 3, in which R₁ and R₂ are each hydrogen or a methyl group.

5. Compounds according to claim 1 that are hereinbefore specifically disclosed.

6. A process for the preparation of a compound according to claim 1 (but with the proviso inoperative), in which R is hydrogen, a methyl group or a (C₁—C₄-alkoxy)carbonyl radical, which process comprises reacting an

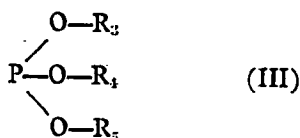
N - acylamino - methyl compound of the general formula



in which

- 5 R' has the meaning stated above for R, R₁ and R₂ have the meanings stated in claim 1, and

- 10 X represents a halogen atom, an hydroxyl, dimethylamino or diethylamino group or an acetoxy or propionyloxy radical, with a phosphorous acid triester of the general formula



in which

- 15 R₃, R₄ and R₅ each represent, independently of one another, a C₁-C₄-alkyl radical which is optionally substituted by one or more halogen atoms, or

- 20 R₃ and R₄ alternatively form, together with the adjacent oxygen atoms and the phosphorous atom, a five-membered to seven-membered heterocyclic structure,

optionally in the presence of an inert diluent, at a temperature of from 40° to 160°C.

- 25 7. A process according to claim 6, in which R is hydrogen and R₁ and R₂ are each hydrogen or methyl.

8. A process according to claim 6 or 7, in which X is chlorine or hydroxyl.

- 30 9. A process according to claim 6, 7 or 8, in which the reaction is effected at from 60° to 130°C.

10. A process according to claim 6 or 7, in which X is an acetoxy or propionyloxy radical.

- 35 11. A process according to claim 10, in which the reaction is effected at from 90° to 150°C.

- 40 12. A process according to any of claims 6 to 11, in which R₃, R₄ and R₅ are identical and each represent a methyl, ethyl or chloroethyl group.

- 45 13. A process according to any of claims 6 to 12, in which the compound of the formula (II) is one that is hereinbefore mentioned.

- 50 14. A process according to any of claims 6 to 13, in which the compound of the formula (III) is one that is hereinbefore mentioned.

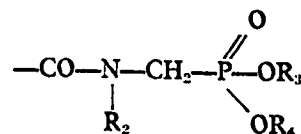
15. A process according to any of claims 6 to 14, in which the compound of the formula (II) and the compound of the

formula (III) are employed in a molar ratio of 1:1 to 1:2.

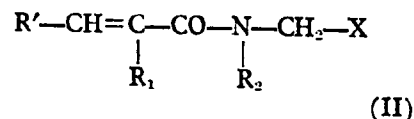
- 55 16. A process according to claim 6, substantially as hereinbefore described and/or exemplified.

17. Compounds according to claim 1 whenever prepared by a process according to any of claims 6 to 16.

18. A process for the preparation of a compound according to claim 1, in which R represents a radical of the formula

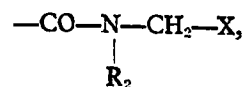


which process comprises reacting a compound of the general formula



in which

R' represents a radical of the formula



and

R₁, R₂ and X have the meanings stated in claim 6, with a phosphorous acid triester of the formula (III) as defined in claim 6, optionally in the presence of an inert diluent, at a temperature of from 40° to 160°C.

19. A process for the preparation of a compound according to claim 1, in which R₃ and R₄ represent a hydrogen atom or an alkali metal, alkaline earth metal or ammonium ion, which process comprises hydrolysing a corresponding alkyl ester and, if required, neutralizing the acid so formed.

20. A compound according to claim 1 whenever prepared by a process according to claim 18 or 19.

21. A method of flame-proofing a textile, paper or plastics material which comprises incorporating into the said material a compound according to any of claims 1 to 5 and 17.

22. A method according to claim 21 substantially as hereinbefore described and/or exemplified.

23. A method of flame-proofing a textile, paper or plastics material which comprises incorporating into the said material a compound according to claim 20.

24. A textile, paper or plastics material

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whenever flameproofed by a method according to claim 21 or 22.

25. A textile, paper or plastics material
whenever flameproofed by a method according to claim 23.

For the Applicants,
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